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(54) Title: FLOOR COVERING		
(57) Abstract  The present invention relates to sheet materials suitable for use in or as a floor covering. The sheet materials comprise a polyalkene resin in intimate admixture with at least one additive comprising a filler, wherein the polyalkene resin has a relatively narrow molecular weight distribution (MWD), and a small amount of long chain branching and produced by a single site catalysed polymerisation of at least one, linear, branched or cyclic, alkene having from 2 to 20 carbon atoms. The present invention also extends to processes for the production of such sheet materials and floor coverings.		

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FLOOR COVERING

The present invention relates to floor coverings and more particularly to durable tile or sheet form floor coverings made of one or more layers of polymers suitable for e.g. pedestrian traffic in domestic and/or other situations over an extended period of time.

Most floor coverings of this type are based on polyvinylchloride (PVC) polymer. In more detail, PVC polymer resin is generally mixed with a plasticiser (solid or liquid) (usually with various other additives such as fillers, polymer stabilisers, and processing aids) to form a spreadable paste which can be formed into sheets by spread coating using knife or roller coater equipment and then thermally cured e.g. by oven heating.

The use of PVC does however raise significant environmental problems due to the use of chlorine and there is accordingly a need for floor coverings based on alternative polymers. Polyalkene polymers are generally preferred from an environmental point of view but the use of conventional polyalkenes presents significant processing problems and they are not suitable for use in floor covering manufacturing facilities based on spread coating and calendaring technology. In addition a particular problem in employing conventional polyalkene polymers in floor coverings, is that they do not provide the necessary physical characteristics required in the final product. In more detail floor coverings produced using conventional polyalkenes have been known to give insufficient tensile and tear strength, abrasion and stain resistance, and elastic recovery.

30

It is an object of the present invention to avoid or minimize one or more of the above disadvantages.

It has now been found that a particular class of polyalkenes, which are produced by single site catalysed polymerisation, can be successfully used in floor covering manufacture based on more or less conventional spread

coating or calendering technology. More particularly, suitable polyalkenes in accordance with the present invention are those having a relatively narrow molecular weight distribution (MWD) and, a small amount of long chain branching and produced by single site catalysed polymerisation, and having the following characteristics:

- a) Melt Index (MI) of from 0.1 to 100
- b) Density of from 0.86 to 0.97; and
- c) a DRI of from 0.1 to 6.0, preferably from 0.4 to 5.5.

10 As used herein the following terms have the meanings indicated:

Melt Index (MI) or  $I_2$  is the amount (in grams) of polymer resin which is extruded in a predetermined period of time (10 minutes) as measured in accordance with ASTM (American Standard Testing Method) D-1238 (190/2.16).

Molecular Weight Distribution (MWD) is the ratio of weight average molecular weight ( $M_w$ ) to number average molecular weight ( $M_n$ ) (i.e.  $M_w/M_n$ ).

Density is the mass (in grams) of 1 cubic centimetre of resin as measured in accordance with ASTM D-792 standard.

Dow Rheology Index (DRI) is an index of long chain branching measured by comparing the shift to the right (due to a longer relaxation time), relative to a polymer resin with zero long-chain branching (LCB), in a plot of zero shear viscosity against relaxation time (both from a cross viscosity equation).

Other abbreviations used herein which are common in the art include:

PHR - parts per hundred parts by weight of polymer resin (or principal polymer resin component).

Suitable polyalkenes in accordance with the present

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invention may also comprise a polyalkene having a relatively narrow molecular weight distribution (MWD) and, a small amount of long chain branching and produced by a single site catalysed polymerisation of at least one, linear, branched  
5 or cyclic, alkene having from 2 to 20 carbon atoms.

Conveniently the polyalkene comprises a copolymer produced by copolymerisation of two or more alkenes comprising a first linear or branched, alkene having from 2 to 8 carbon atoms and, a second, linear, branched or cyclic, alkene  
10 having from 2 to 20 carbon atoms. This allows for greater design flexibility in relation to obtaining sheet materials with particular desired combinations of physical characteristics. In general there may be used up to 15 mole percent of said second monomer. It will of course be  
15 understood that where cyclic alkenes are used these may have more than one carbon ring and thus include bicyclic and tetra-cyclic alkenes such as norbornene and tetracyclododecene.

In another aspect the present invention provides a sheet  
20 material suitable for use in or as a floor covering and comprising a polyalkene resin in intimate admixture with one or more additives selected from a filler and a spread coating processing aid, wherein said polyalkene resin has a relatively narrow molecular weight distribution (MWD),  
25 preferably less than 3.0, and, a small amount of long chain branching and produced by single site catalysed polymerisation, and having the following characteristics:-  
a) Melt Index (MI) of from 0.1 to 100  
b) Density of from 0.86 to 0.97; and  
30 c) a DRI of from 0.1 to 6, preferably 0.4 to 5.5.

One of the very versatile features of metallocene catalysts is the range of comonomer which may be incorporated into polymeric chains by using such catalysts in the single site polymerisation of alkenes. Metallocene catalysts are, for  
35 example, capable of incorporating into polymer chains cyclic monomers, advantageously polycyclic monomers, including cyclic monomers such as norbornene ( $C_7H_{10}$ ). Thus, for

example it is possible to incorporate materials such as norbornene into copolymers with ethylene, which has the benefit of raising the toughness and melting point over conventional PE resins.

- 5 The new sheet materials provided by the present invention have the further advantage of suitability for incorporating various design features. It may be possible to incorporate graphic images into the flooring in a manner which will give an image with depth perception. Systems using ion  
10 projection technology are well known in the art. These systems use an electrostatic charge corresponding to the desired image. This image is deposited on the material with a drum or belt. The material bearing the electrostatic image is moved through a developer station where a toning  
15 material opposite charge adheres to the charged areas of the dielectric surface to form a visible image. Another layer of polymer may be deposited on top of this, and another image produced in this layer. By adding successive layers, each with its own image, it is possible to build a structure  
20 with an image depth perception. This art, using conventional resins, is explained in US 5347296.

- One advantage of using polymer prepared using metallocene-derived catalysts comes about during the image process. More particularly the use of metallocene catalysts permits  
25 the incorporation of boron containing end groups and/or very high levels of unsaturation. These end groups may be functionalized to provide additional means for facilitating imaging. Images may be created either via electrostatic projection systems or by functionalizing these end groups so  
30 the polymer chains will better combine with toner or pigments.

- In another aspect the present invention provides a sheet material suitable for use in or as a floor covering and comprising a polyalkene resin in intimate admixture with at  
35 least one additive comprising a filler, wherein said polyalkene resin has a relatively narrow molecular weight

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distribution (MWD) and, a small amount of long chain branching and produced by single site catalysed polymerisation of a first, linear or branched alkene having from 2 to 8 carbon atoms and, preferably a second, linear, 5 branched or cyclic, alkene having from 2 to 20 carbon atoms.

Whilst processing aids may be used in the new materials of the present invention, to adjust or accentuate particular processing characteristics such as reduced energy requirements and/or increased processing speed, it is a 10 feature of the polyalkene resins used in the present invention that they do not require the use of a plasticiser thereby significantly reducing environmental problems caused by the migration of liquid plasticizers out of the material and/or loss of performance associated with the use of 15 plasticisers.

Nevertheless, in those cases where it is desired to increase processability, then there may be used a processing aid or plasticiser, and it is an advantage of the present invention that a significantly smaller amount of plasticiser can be 20 used as compared with polymer resins conveniently used in floor coverings. In a particularly preferred form of the invention there is, moreover, used a plasticiser or processing aid comprising a selectively polymerisable liquid monomer system which is substantially non-polymerisable 25 under the sheet forming, e.g. extrusion, spread-coating or calendering, conditions used in the floor covering sheet material manufacturing process whilst being substantially polymerisable subsequently so as to produce a material substantially free of liquid plasticiser. In general the 30 polymerisable monomer may be used in an amount relative to the polyalkene resin of from 20 to 80 : 80 to 20. Further details of suitable plasticisers are discussed hereinbelow.

In this connection it will be understood that there is normally used an initiator substance in order to induce 35 polymerisation of the monomer and which is included together with the monomer in the monomer system. Accordingly in such

cases it is important that the initiator is one that is selectively activatable i.e. is substantially inactive under the polyolefin product forming conditions but may subsequently be activated under suitable plasticiser monomer polymerisation or curing conditions.

Various polyalkene resins suitable for use in the materials of the present invention are known in the art. In general they are produced by polymerisation of alkene monomers in the presence of particular catalysts which restrict the progress of the polymerisation and are known as metallocenes (the resulting polymers being commonly referred to as metallocene polyolefines conveniently abbreviated as MPOs). Such polyolefines and processes for their production are described in, inter alia, US Patent 5,272,236.

- 15 Preferred polyalkenes that may be mentioned comprise copolymers of ethylene and an  $\alpha$ -alkene having from 4 to 20 carbon atoms, advantageously from 4 to 10 carbon atoms, for example propylene butene-1, or hexene-1, or a cyclic olefine such as norbornene; copolymers of propylene and an
- 20  $\alpha$ -alkene having from 2 to 10 carbon atoms, for example butene-1, hexene-1, or a cyclic olefine such as norbornene; and copolymers of 4-methyl-1-pentene and an  $\alpha$ -alkene having from 2 to 10 carbon atoms, for example, butene-1, hexene-1, or a cyclic olefine such as norbornene.
- 25 Preferably there is used a copolymer containing up to 15 mole percent of comonomer. It will moreover be appreciated that there may be used more than one comonomer, that is, there may for example be used a terpolymer wherein are employed two different  $\alpha$ -alkenes each having from 2 to
- 30 20 carbon atoms.

Suitable polyalkene resins that are commercially available from the Exxon Chemical company of USA and the Dow Chemical company of Midland, Michigan, USA, are listed in Tables 1 and 2 below.



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<u>Product</u>	<u>Key Properties</u>
EXACT 3017	Density 0.901 MI 27
5 EXACT 3025	Density 0.910 MI 1.2
EXACT 4038	Density 0.885 MI 125
EXACT 4041	Density 0.878 MI 3.0
10 EXACT 5008	Density 0.865 MI 10
EXACT 4006	Density 0.880 MI 10.0
15 EXACT 4003	Density 0.895 MI 9.0
EXACT 4023	Density 0.882 MI 35.0
20 EXACT 4033	Density 0.880 MI 0.80

Table 2 - Dow's INSITE (TM) TECHNOLOGY POLYMER (ITP)

<u>Product</u>	<u>Key Properties</u>
Engage CL8200	Density 0.870 MI 5.0 DRI 0.5
25 Engage CL8150	Density 0.868 MI 0.5

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	DRI	2.0
Affinity SM1300	Density	0.902
	MI	30.0
	DRI	0.4
5 Affinity SM1250	Density	0.885
	MI	30.0
	DRI	--
Engage LG 8005	Density	0.870
	MI	1.0
	DRI	2.0

10

In a further aspect the present invention provides a polymer resin-based floor covering comprising at least one layer of a sheet material of the invention. It will be appreciated that in general such floor coverings comprise two or more  
15 different layers having particular functions, bonded together. Typically there may be included layers such as a foamed layer to provide cushioning; a structural layer comprising a reinforcing carrier or substrate impregnated and/or coated with a saturant formula; a solid backcoat  
20 layer; and a clear protective or topcoat layer.

For some types of applications little or no expansion in some or all layers of the floor covering structure will be required. The current invention includes a range of floor covering systems from those wherein all layers, except the  
25 topcoat, are foamed to those where none of the constituent layers are foamed.

The sheet materials of the invention may be produced by a process comprising the steps of:  
providing a suitable polyalkene resin in accordance with the  
30 present invention and at least one additive comprising a filler and optionally a sheet formation, typically a spread coating or calendering, processing aid;  
bringing said polyalkene resin into intimate admixture with

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said at least one additive in a high shear mixer for a period of at least 10 minutes at an elevated temperature of at least 75°, preferably from 100 to 250°C, most preferably from 130 to 200°C, for melting the polyalkenes and  
5 sufficient to bring the mixture into a substantially fluid state without substantial degradation of the mixture; forming the fluid mixture into a sheet form; and allowing said sheet to cool and solidify.

In one preferred aspect of the invention there is used a  
10 said fluid mixture which is substantially free of any plasticiser. Nevertheless, as discussed elsewhere herein, there may be included in the mixture one or more plasticisers or processing aids. Where there is used a polymerisable plasticiser, then the process includes further  
15 treatment of the solidified sheet in order also to solidify the plasticiser. Where a fugitive plasticiser is used the process advantageously includes the step of volatilizing said plasticiser.

The sheet material production processes of the present  
20 invention have significant advantages over those made using conventional polyalkene or polyolefin resins. Apart from the superior processability which allows the use of conventional existing production plant previously utilized for PVC resin based sheet materials with minimal  
25 modifications, they also have lower energy consumption costs due to the substantially reduced curing temperatures required as compared with PVC resin based production which involve increasing temperature to effect a thermal curing as opposed to a cooling to effect "crystallisation curing" by  
30 "solidification". Further benefits that can be obtained in relation to particular floor covering layers in products of the invention include better toughness of the outer clear coat layer with better impact resistance resulting from the lower crystallinity associated with lower density; better  
35 cell recovery in foamed cushioning layers; and better filler acceptance due to more homogenous nature of the polymer (narrow MWD); and good flowability of the saturated layer

resulting from high MI with little or no comonomer blocking.

In relation to the various aspects of the present invention it will be appreciated that other polymer resins outside those specified may be used in admixture with the specified  
5 ones e.g. in order to "extend" the specified polyalkene resin for reasons of economy by using a cheaper polyalkene resin, or to modify finish or other characteristics. The amount of such other polymer resin that may be used will depend primarily on how they affect the fluidity and spread  
10 coating characteristics of the materials of the invention. Thus for example there may be used up to around 50 to 60%w/w of said other polymer resin (relative to the total polymer resin) depending on the required use and properties of the sheet layer. Thus, for example, in relation to the clear  
15 coat layer, the amount of such other polymer resin would normally be restricted to a lesser amount of not more than around 15 to 20%w/w.

Additives that may be used in the materials of the present invention and the amounts thereof, will depend on the  
20 function and desired properties of the sheet material and may also, to some extent, depend upon the particular polymer resins used. Principal additives and additional processing steps generally well known in the art, that may be mentioned include the following:

25 1. Inorganic fillers and reinforcements can enhance the various polyolefin based layer or layers in the floor covering material, which is the subject of this invention. This enhancement can be through improvements in appearance, physical properties, or chemical characteristics. The  
30 particular inorganic filler/reinforcement attributes that are important are the nature of the inorganic material, the shape of the material, and any surface treatment or coating. There are many important aspects of the inorganic material. Density is important in the application and long term  
35 utility of a floor covering. Highly filled back coat layers (e.g. up to 85% by weight of filler) can be very useful in

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this regard. Another basic material attribute is hardness. Increased hardness is desirable in the final product, but too hard a filler (such as silica) can have negative effects on the wear of processing equipment, such as melt mixers and extruders. Table A lists some common inorganic fillers/reinforcers.

**TABLE A**

INORGANIC MATERIAL	DENSITY g/cc	HARDNESS MOBE SCALE
Calcium Carbonate	2.7	3
10 Talc	2.9	1.5
Mica	2.8	3
Glass Fibres	2.9	--
Silica	2.5	7.0
Wollastonite	2.9	4.7
15 Aluminium Trihydrate	2.4	3.0
Magnesium Hydroxide	2.3	2.0
Titanium Dioxide	4.2	7.0

Whiting filler is used to increase opacity. Generally there is employed less than 500 PHR, preferably from 20 to 120 PHR in saturant formula and foamable cushioning materials and up to 200 PHR in solid backing layers.

The optical properties of titanium dioxide make it a particularly good pigment in obtaining a white colour with good opacity. Such a colour is desirable in the layer upon which the printed design is placed. This is located below the transparent wear layer. Lower levels of titanium dioxide (2 to 6 PHR) can be employed if a white filler such as Calcium carbonate is used at moderate levels in this layer.

Calcium carbonate is of particular utility in polyolefin based compositions. Hardness, stiffness, heat deflection temperature, slip resistance, stress crack resistance, weldability, printability, and antiblock characteristics are all improved. Thermal shrinkage and elongation, as well as water vapour and oxygen permeability are decreased.

Talc is another filler well suited to enhance polyolefin formulations for floor covering. It has a lamellar structure in contrast to the low aspect particulate structure of calcium carbonate. This lamellar form allows talc to be more effective than calcium carbonate with regard to increasing stiffness, heat deflection temperature and dimensional stability. The disadvantage of talc relative to calcium carbonate centre on reduced impact strength, matt surface, and lower thermooxidative stability. Mica also has a lamellar structure and has similar advantages and disadvantages.

High aspect ratio fillers/reinforcements such as wollastonite and glass fibres, have an even stronger effect than talc and mica on increasing the modulus of elasticity, tensile strength, and heat-distortion temperature of polyolefin based systems.

The improvements provided by high aspect ratio inorganic additives would be of particular assistance in these floor covering systems made using a permanent plasticizer or processing aid, such as liquid paraffin. In these cases, the stiffening action of such additives would compensate for the loss of stiffness produced by the liquid paraffin.

Silica in its fumed or precipitated forms can be useful at low levels (0.1 to 1.5%) in the polyolefin formulations where antiblocking and printability is of importance. In the floor covering system these would be in the wear layer and in the layer upon which the printed design is applied.

Alumina trihydrate and magnesium hydroxide, in the correct

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particle sizes which for most systems are less than 40 microns in diameter, can provide the same type of property enhancement provided by calcium carbonate. In addition, they can provide useful fire resistance and smoke control characteristics. This will be discussed in more detail in the fire resistance section.

2. Polyolefin materials for floor covering systems are enhanced by the use of the thermal and light stabilizers. For thermal stabilizers the amount and type that should be used will vary with the actual process used to fabricate the final structure. The melt spreader approach will provide a product having less heat history than either the melt calendaring or extrusion routes. In all cases that involve foamed systems, however, the polyolefin resins will be exposed to temperatures over 180°C for some time during the process.

Suitable stabilisers include hindered phenol at from 0.05 to 0.30 PHR, optionally with co-stabilisers e.g. organosulphur compounds such as DSTDP at from 0.2 to 1.0 PHR. More particularly good thermal stability can be obtained in these polyolefin systems using a high molecular weight hindered phenol, such as Irganox 1010 from Ciba-Geigy, with one or more secondary antioxidants such as thioethers and phosphorus compounds. Distearylthiodipropionate (DSTDP) and Ultrinox 626 from GE are examples of these types of materials. An effective thermal stabilizer package from such systems is 0.1% Irganox 1010, 0.1% DSTDP and 0.05% Ultrinox 626.

Hindered amine light stabilizers (HALS) are particularly effective in protecting polyolefins from photo-oxidation. A Polymeric HALS, such as Luchem HA-B18 from Atochem, is particularly effective in its own right and has the added advantage of showing no antagonism for other additives such as DSTDP. The inclusion of 0.3% of Luchem HA-B18 in the outer wear layer and 0.15% in the layer just below the transparent wear layer will greatly enhance the light

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A supplemental blowing agent such as aluminum trihydrate may be employed in these structures. Although its primary role is that of a flame retarding additive and inorganic filler it has a useful auxiliary role as a blowing agent in that it gives off water vapour when heated above 200°C. A volatile fugitive processing aid or plasticizer can also have a useful role as a supplemental blowing agent.

In the case of azodicarbonamide this is generally used for foamable cushioning layers at from 2.0 to 4.5 PHR, together with a suitable foaming activator such as zinc oxide.

Some or all chemical blowing agents can be replaced with mechanical foaming, given the correct conditions. Such conditions involve the mixing into the polyolefin based mixture, that will become one of the layers in the floor covering material, air or another gas, under conditions that will produce the desired number and size of cells in the resulting foam. In the spread coating system the mixture as applied needs to have a foam structure near to that of desired product. In the extrusion or calendering process the gas needs to be in solution in the polymer or as small micro bubbles at the melt pressure in the extruder system. Expansion takes place as the melt leaves the extruder and goes from high pressure (100 to 700 PSI) to atmospheric pressure. In both cases, it is important for the cell structure to be frozen at the desired size by a rapid drop in the sheet temperature to below that needed for cell contraction or deformation.

6. The properties of the polyolefin structures in the subject floor coverings can be enhanced through the use of crosslinking, conveniently by means of an organic peroxide e.g. at from 0.1 to 5.0 PHR for increasing toughness and/or stiffness of the sheet layer. Dicumyl peroxide is a reagent used extensively for such reactions. This material becomes an effective crosslinking agent at 190°C. In the case of crosslinked foamed polyolefin systems it is known that a better foam cell structure is developed if the crosslinking



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is done before the foam is formed. In systems involving Celogen AZ for foaming and dicumyl peroxide for crosslinking, both processes would take place at the same time and temperature. If a peroxide with a lower activation temperature, such as 2,2-bis (tert. butylperoxy) butane were used then the crosslinking could be carried out at about 170°C followed by a foaming process at 190°C.

The development of strong crosslinked filled foam polyolefin systems can be further enhanced by treating the inorganic filler to be used with vinyl silane. The vinyl groups that become attached to the filler particles become active in forming the cross linked network initiated by the peroxide produced free radicals.

In non-expanded layers Dicumyl peroxide would be a good crosslinking agent. In layers to be expanded, using 2,2-bis (tert. butylperoxy) butane in conjunction with an activated Celogen AZ blowing system would be desirable. In all filled layers to be foamed, the filler should be treated with an agent such as vinyl silane that will provide sites of unsaturation on the filler particles.

7. The flammability and smoke generation of the polyolefin based floor covering system is of importance. Fire characteristics can be improved through a wide range of additives. Various inorganic compounds, such as aluminum trihydrate and magnesium hydroxide, that give off water at elevated temperatures are useful as dual fillers/flame retardants. Phosphorous compounds, borates, and zinc oxide all can play useful roles in improving the fire characteristics of polyolefin bases systems.

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8. polymer resins other than the specified MPOs may be used as noted above as extenders or modifiers in amounts of from 10 to 30 PHR. Examples that may be mentioned include LLDPE (Linear Low Density PolyEthylene), EVA (Ethylene Vinyl Acetate), Ionomers e.g. SURLYN (TM) available from the DuPont Company, and VLDPE (Very Low Density PolyEthylene).

In addition, blends of two or more metallocene prepared polyolefins may be used to obtain particular combinations of desired properties.

- 10 To improve impact properties various types of elastomeric component additives can be used in generally known manner. These generally comprise small particles with a core of an elastomer e.g. butadiene or acrylic polymer coated with an outer shell that will provide good adhesion to the MPO
- 15 polymer resin matrix. An example of such an elastomeric component core/shell modifier additive is Paraloid EXL-330 from the Rohm and Haas Company. This resin has an acrylate rubber core and a polymethyl methacrylate shell. Other types of modifiers that can be used to enhance impact
- 20 properties include EPDM rubbers, such as Polysar manufactured by Bayer; A/B/A block copolymers, such as Kraton manufactured by Shell; and multiple domain elastomer systems, such as those described in European Patent No. 583,926.
- 25 9. Other additives that may be mentioned include dyes, inks, antioxidants etc. which are generally used in relatively small amounts at less than 50 PHR. Antistatic characteristics can also be important for some applications.

In this case, the use of various internal antistatic agents in the wear layer would be appropriate. Many antistatic additives are compounds with hydrophilic and hydrophobic sections. A common material of this type is a mono ester of  
5 a polyol, such as glycerol, with a long chain fatty acid, such as stearic acid. The polyol portion is very polar and would come to the surface of a polyolefin, while the fatty acid is "polyolefin-like" and would stay within the plastic.  
9. The hydrophilic part can be cationic, anionic, or non-  
10 ionic. Levels of 0.1 to 0.5 PHR in the outer layer of the structure are appropriate.

10. Carriers or substrates used with saturant formulations may have various forms e.g. woven or non-woven mesh or fabric, or tissue, of more or less thermally stable  
15 materials such as glass fibre.

The polyalkene or polyolefin resins used in accordance with the present invention may be of various different types including random bipolymers and terpolymers, and block copolymers, based on a variety of monomer units including  
20 lower alkene, preferably 1-alkene, having from 2 to 8 carbon atoms e.g. propylene but most preferably ethylene; dienes; cycloalkenes; and vinyl aromatic compounds.

Further preferred features of the invention will appear from the following detailed Examples given by way of illustration  
25 and the accompanying schematic drawings in which:

Fig. 1 is a schematic side view showing a first part of a floor covering production line; and

Fig. 2 is a similar view of the second part of the production line of Fig. 1.

30 Fig. 1 shows a first-stage production line 1 for producing a first-stage three layer sheet material 2 by applying saturant, foam gel, and back-coat layer formulations 3, 4, 5 onto a glass fibre tissue web (approx. 0.45 mm thick) 6 supplied from a supply drum 7 via a first accumulator 8.  
35 The tissue web is passed via a first weight/unit area

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measuring system 9 to a first spread coating unit 10 at which the hot melt saturant formulation 3 (at approx. 90°C) is applied onto one side 11 of a first roller 12 to a predetermined thickness of about 0.55 mm controlled by a first knife 13, from a first continuous high shear barrel-type mixer 14. At the other side 15 of the first roller 12, the saturant formulation is transferred to the tissue web 6 at a nip 16 between the first roller 12 and an opposed tissue web support roller 17. The impregnated tissue web 18 is then passed around a large diameter chilled drum 19 set for a surface temperature of around 25 to 40°C and further smaller diameter cooling drums 20 for "crystallisation curing" or solidification.

The hot melt foam and back-coat layer formulations 4, 5 are then successively applied to the coated tissue web 18 at approximate thickness of 0.2 and 0.6 mm, respectively, in generally similar manner at second and third spread coating units 21, 22, except that a large diameter chilled drum 19 is omitted at the back-coat layer stage. The resulting three layer sheet material 2 is then collected on a wind-up drum 23 down-stream of a second accumulator 24. If desired this sheet material is then passed to a rotogravure or other printing station for application of graphic design material etc. in generally known manner, for example, using ink designed for chemical embossing.

Fig. 2 shows a second stage production line 101 in which like parts corresponding to those in Fig. 1 are indicated by like reference numerals to which have been added 100. The three layer sheet material 2 produced in the first stage production line 1 is supplied from a supply drum 107 via an accumulator 108 to a fourth spread coating unit 110 at which a clear coat formulation 125 is applied to said sheet material 2 at a thickness of about 0.2 mm, and cured as before except that in this case a heat shield 126 is provided between the chilled drum 119 and the hot mixer 114 to help improve temperature control etc.

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If desired a further foamed back-coat layer may be applied using yet another spread-coat applicator (not shown). It will incidentally be appreciated that in accordance with common practice in the industry the order of application of the various layers can be varied to a greater or lesser extent.

Finally where a polish or lacquer type finish is required this can be applied using a grooved roller applicator 127.

The resulting multi-layer sheet material 140 is then passed through a multi-stage hot air oven 141 on a belt support 142 set to a maximum temperature of around 200°C with a dwell time of around 1½ minutes to allow foaming expansion of the foam layer (from about 0.2 mm to about 0.5 mm) with selective control thereof by chemical embossing where this is used, whereupon final cooling of the finished sheet material takes place at further cooling drums 120 prior to collection on the take-up drum.

Melt calendering can also be used to produce the floor coverings which are the subject of this invention. Although both rolling sheet and viscous blank calendering can be employed, rolling sheet is preferred with a glass fibre web, being the preferred substrate.

A multilayer laminate is prepared by applying a series of melts based on the polyalkene or polyolefin resins as described in this invention. These melt calendering operations can all be done in a continuous way using a series of calendering rolls, or they may be done in a segmented fashion with a single layer being applied followed by a wind up operation with additional layers being added in separate operations. In addition, a combination of continuous and discontinuous calendering operations can be employed. Thus for example, a saturant formulation can be applied to a glass fibre web followed by a foamable layer or top and a base layer beneath. These three operations being carried out in a consecutive way as the material passed

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through three different sets of calender rolls before wind up. Additional processing steps can be placed between and among calendering operations. For example, the material produced by applying three polymer layers to a glass fibre web could be passed through a printing process, to provide a decorative image and to facilitate chemical embossing. This distinct printing step could be followed by another melt calendering step to apply a wear layer to the floor covering. A heat treatment step could follow the application of the wear layer, either in a continuous or discontinuous fashion. The heat treatment could expand the various layers through the formulation of a chemical foam, in those layers containing a chemical blowing agent. In addition, the physical and chemical properties of the polyolefin resins could be enhanced through crosslink formation in these layers via the use of a crosslinking system.

In the melt calendering process, a polymer melt is applied to a series of two or more heated rolls in such a way to produce a layer of polymer of uniform thickness. The melt is prepared by mixing the polymers and non-polymeric components of the material under conditions of elevated temperatures and shear. Devices such as extruders or mixers can be used for this process. More detailed descriptions of the melt calendering process can be found in Chapter 83 of "Handbook of Plastic Materials and Technology" by Irvin I. Rubin and published by John Wiley and Sons, Inc (ISBN 0-471-09634-2)

The floor covering structure, which is the subject of this invention, can also be prepared by melt extrusion. In such a process, one or more polymer layers can be applied to a continuous glass fibre web in a single extrusion operation. When co-extrusion is used to provide multiple layers in a single pass, a separate extruder is used to feed each melt to the sheet die block. Extrusion operations can be intermixed with other processing steps in preparing the final structure. For example, a glass web can be saturated

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- and encapsulated between a base layer and foamable layer in single co-extrusion pass involving a three melt feed sheet die. This structure then can be subjected to a printing process followed by a single layer being added by extrusion.
- 5 A thermal treatment can follow the application of the wear layer in either a continuous or discontinuous fashion. This treatment could enhance the final product by expansion of layers containing chemical blowing agents and/or crosslinking of layers containing crosslinking systems.
- 10 The initially described process for developing the desired floor covering structure through the use of a melt spreading approach, as shown in figures 1 and 2, can be extended in scope through the use of fugitive and/or permanent processing aids or plasticizers. This involves the addition
- 15 of a liquid or liquids to the various polyolefin formulations used to make the discrete layers of the final structure. Such an addition can be used to lower the temperature needed to obtain the viscosity needed for good processing. For example, white spirit, petroleum ether, or
- 20 mineral spirits can be blended with a polyolefin layer system using heat and shear mixing to produce a homogenous low viscosity material which can be processed at a lower temperature than would otherwise be possible. This is a fugitive system as the white spirit or other plasticiser
- 25 evaporates from the surface of the structure after the system has been applied. Preferably, the vaporized white spirit or other plasticiser is captured, condensed, and recycled. Alternatively, a non-volatile liquid plasticiser, such as liquid paraffin (mineral oil) can be used. In this
- 30 case, the resulting floor covering structure will retain this material as a permanent component. Mixed systems of fugitive and permanent liquids can also be used. The range for such additives can extend from 200% to less than 5%, on a weight basis of polyolefin. Most desirably though there
- 35 is used a polymerisable plasticiser.

The polymerisable plasticiser monomers that can be used in accordance with the present invention are those that are

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solvents for the main polymer component(s) of the polyolefin product. They need not, and would normally not, be solvents for the inorganic components nor for other components, which may themselves also be polymers, such as impact modifiers, 5 texturing aids, pigments, and some compatibilizers. The monomers will, in general, have a long segment that is "polyolefin like" with an end group that is capable of free radical polymerization. Typical "polyolefin like" structures are hydrocarbons with ten or more carbon atoms, 10 and examples of such groups would be lauryl ( $C_{12}H_{25}$ ) and stearyl ( $C_{18}H_{37}$ ). Such structures can be linear, branched, or cyclic; depending in part upon the structure of the polyolefin. The terminal polymerizable group can be a simple unsubstituted double bond, such as in 1-dodecene or a 15 more complex unit such as a methacrylate, as in stearyl methacrylate.

Along with the plasticiser monomer or monomers, compounds that generate free radicals at elevated temperatures and optionally crosslinking monomers may be used to cure the 20 resulting products and to provide enhanced properties. Many classes of free radical generators can be used, but materials in the peroxide, ketone peroxide, peroxydicarbonate, peroxyester, hydroperoxide, and peroxyketal families are of particular use. Also of utility 25 are several classes of azo compounds and a variety of photoinitiators. The characteristics needed in these compounds is that they are substantially non-polymerisable i.e. remain essentially dormant during the initial mixing, compounding, and product fabrication process but can be 30 induced to produce free radicals at a rate that will initiate a polymerization of the monomer e.g. when the temperature is increased, or when exposed to the appropriate radiation. For example a material such as t-butyl perbenzoate has a half life of over 1000 hours at 100 C, 35 while having a half life of less than 2 minutes at 160 C. In a polymer/monomer system containing such an initiator it would be possible to process the system into the finished product form (i.e. shape or configuration) at 100 C and then



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cure the system by a brief exposure at 160 C.

When polyfunctional monomers are included in the system then a continuous crosslinked polymer system can be formed from the monomer. Optionally additional radical generators can  
5 be included that will provide cross linking of the pre-existing polyolefin system. A Semi-IPN (inter-penetrating network) is obtained when one of the co-continuous systems (i.e. the pre-existing polyolefin and the polymerised plasticiser monomer) is crosslinked. When both systems are  
10 crosslinked an IPN is formed.

To prevent premature polymerisation of the plasticiser monomer it may be useful to add additional inhibitors to the system. Most commercial monomers are provided with inhibitors to prevent polymerization during handling and  
15 processing. The level of such inhibitors should be increased to compensate for the time spent under the polyolefin polymer product forming conditions, i.e. the conditions used to form the base polyolefin polymer into a sheet or some other shape or configuration. In this  
20 connection the temperature is usually the most significant factor, but other conditions may also be relevant. Thus for example stearyl methacrylate is commercially provided with 275 parts per million (ppm) of the monomethyl ether of hydroquinone (MEHQ). Depending on the times and temperature  
25 involved 1000 ppm MEHQ, or more, may be needed. Inhibitors from a wide range of chemical families may be used for this purpose.

The polymeric system and the monomeric system can be combined in a variety of ways to give a low viscosity  
30 plasticised material that can be used to manufacture many types of products using several different fabrication techniques. The combination of the solid and liquid components can be done in any suitable manner e.g. by using a continuous or batch mixer, various types of continuous and  
35 batch blending devices, and various types of extruders. In all these types of equipment the solid components are mixed

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together at sufficient temperature and with sufficient shear to achieve both distributive and dispersive mixing. The liquid is introduced at the needed temperature and shear to dissolve the principal polymeric components and to obtain  
5 good distributive mixing and dispersive mixing of the insoluble components with the resulting fluid. The fluid system is then held at a temperature that retains the required fluidity for the fabrication of the final product form. In general this will ususally be in the from 80 to  
10 120°C.

It will be appreciated that polymerisation of the polymerisable liquid plasticiser will result in the creation of polymer chains which extend through and interpenetrate the previously formed network of MPO polymer chains. Where  
15 both the MPO polymer chains and the polymerised plasticiser are cross-linked then the two polymer materials captively interengage each other forming a so-called interpenetrating polymer network (IPN), whilst if only one of these is cross-linked, then the non-cross-linked polymer chains could in  
20 principle be pulled out. The latter type of material is conveniently referred to as a semi-IPN. Such IPN and semi-IPN materials, whilst having generally similar physical properties to those of the other novel materials provided by the present invention, offer further advantages in terms of  
25 improved stain resistance and/or increased resistance to solvents both during installation and in use of the floor coverings provided by the present invention.

**Example 1 - Preparation of Multi-Layer Floor Covering Using Calendering**

30 A floor covering structure is prepared by first developing three layers in a continuous melt calendering operation in a first stage production line (see Fig. 1). In this operation, a continuous glass fibre mat is fed into a through station calendering line. Each station is fed by a  
35 separate melt mixer. At the first station, the glass mat is saturated with composition A. In the next station, the

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backing layer, composition B, is applied. In the third station, the foamable layer, composition C, is applied. The system is then taken up on a take up roll. In a separate operation this system is fed through a printing line where a decorative design is applied to the foamable layer. In a third processing step, this printed material is fed into single melt calendering station in a second stage production line and then into a two zone oven system (see Fig. 2). At the calendering station a clear top coat, composition D, is applied. In the first zone of the oven, which is at 160°C the crosslinking of each layer occurs; in the second zone at 190°C the expandable layer foams. The final product is then collected on a take up roll.

The compositions of the various layers are as follows:-

15	A. ( <u>Saturant Layer</u> )	<u>PHR</u>
	Exact 4038 MPO Resin	100
	Magnesium Hydroxide Fire retardant inorganic filler	60
20	Dicumyl Peroxide free radical source for crosslinking polymerisation	2
	Irganox 1010 hindered phenol thermal stabilizer for reverting polymer degradation manufactured by Ciba-Geigy Corp.	0.1
25		
	DSTDP (Distearylthioldipropionate) thioester secondary antioxidant for preventing polymer degradation	0.1
30		
	Ultranox 626 secondary antioxidant from Berg-Warner Chemicals	0.05

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B. ( <u>Back Layer</u> )		
	Exact 4038	100
	Magnesium Hydroxide	150
	2,2-bis (tert. butylperoxy) Butane free	
5	radical source crosslinking	
	polymerisation	2
	Irganox 1010	0.1
	DSTDP	0.1
	Ultranox 626	0.05
10 C. ( <u>Foamable Layer</u> )		
	Exact 5008	100
	Wollastonite high aspect ratio calcium	
	metasilicate reinforcing filler	30
	Aluminum Trihydrate flame retardant	
15	inorganic filler	30
	Azodicarbonamide chemical foaming agent	
	(giving off nitrogen gas)	2
	Zinc Oxide for lowering decomposition	
	temperature of Azodicarbonamide to reduce	
20	polymer foam temperature	0.8
	2,2-bis (tert. butylperoxy) Butane	2
	Irganox 1010	0.1
	DSTDP	0.1
	Ultranox 626	0.05
25	Luchem HA-B18 polymeric hindered amine	
	light stabilizer from Atochem for	
	preventing polymer photo degradation	0.15
D. ( <u>Top Wear Layer</u> )		
	Exact 5008	100
30	Vinyltriethoxysilane, providing	
	additional crosslinking toughness and	
	solvent resistance	4
	2,2-bis (tert. butylperoxy) Butane	2
	Luchem HA-B18	0.3
35	Irganox 1010	0.1

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DSTDP	0.1
Ultranox 626	0.05

Example 2 - Preparation of Multi-Layer Floor Covering Using Spread-Coating

5 In example 2, the same sequencing of steps and stations are used as in Example 1, except that each application station involves a melt spreading operation rather than a melt calendering operation. The composition of all the four layers is the same except that 80 parts of Jayflex 215 and  
10 20 parts of monomer X980 (a crosslinking monomer from Rohm & Haas) are added to each of the four formulations.

It will be appreciated that various modifications may be made to the above described embodiment with out departing from the scope of present invention. Thus for example  
15 Electron Beam initiated crosslinking can be an alternative or supplemental process to chemically initiated crosslinking. Such crosslinking can be accomplished by subjecting a sample to high-energy electrons at a dose of about 6 to 8 mega rads over a 30 second to 2 minute period.  
20 The addition of a reactive monomer such as methyloolpropane trimethacrylate (TMPTMA) at about 2 to 5 parts is useful to get a good result from this process.

Example 3 - Individual layer formulations

The following polymer resin formulations have been prepared:

25	A. ( <u>Clear coat layer</u> )	<u>PHR</u>
	MPO Resin Engage EP8500 (Dow Chemical Co.)	100
	(MI 5.0, Density 0.87, DRI 0.5)	
	Irganox 1010 Antioxidant Stabiliser	0.05
	BHT Antioxidant Stabiliser	0.03
30	2,5 - TRI Cross-Linking Agent	0.1
	B. ( <u>Foamable Gel Layer</u> )	<u>PHR</u>
	MPO Resin Engage EP 8500 (Dow Chemical Co.)	100
	Whiting filler (generic)	15

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	Azo blowing agent (generic)	3
	Zinc oxide Foaming Catalyst	1.5
	Titanium oxide pigmentation component	4
	Irganox 1010 Stabiliser	0.075
5	DSTDP Stabiliser	0.05
	Calcium stearate Flowing Agent	0.10
	Firebrake (TM) flame retardant	5
	Antimony oxide flame retardant	4
	C. ( <u>Saturant Layer</u> )	<u>PHR</u>
10	MPO Resin Engage EP 8500 (Dow Chemical Co.)	100
	Whiting filler (generic)	50
	Irganox 1010 Stabilizer	0.1
	Zinc stearate Flowing Aid	0.4
	D. ( <u>Solid Backcoat Layer</u> )	<u>PHR</u>
15	MPO Resin Engage EP 8500 (Dow Chemical Co.)	100
	Whiting filler (generic)	200
	Titanium oxide pigmentation component	4
	Irganox 1010 Stabiliser	0.075
	DSTDP Stabiliser	0.05
20	Calcium stearate Flowing Agent	0.10
	Firebrake (TM) flame retardant	5
	Antimony oxide flame retardant	4

#### Example 4 - Individual Layer Formulations

A further set of polymer resin formulations is prepared as  
 25 in Example 1 above but with Dow Chemical Co.'s Affinity SM  
 1250 as the MPO Resin component in place of EP 8500.

#### Example 5 - Preparation of Multi-Layer Floor Covering Using Multiple Spreading

A floor covering material is prepared as a four layer  
 30 structure by a multiple spreading application technique. At  
 an initial station a glass fibre web is saturated with  
 polymer having composition A at a temperature of  
 approximately 100°C. At a separate station a back coating

of composition B is applied to the bottom side of the polymer saturated glass web at approximately 100°C. At another separate station the foamable layer, composition C, is applied to the top side of the polymer saturated glass web at approximately 100°C. A decorative pattern is then printed upon the foamable layer using a continuous printing process that employs, in one of several inks, benzotriazole, to deactivate the accelerated foaming system thereby to produce a chemical debossing effect upon foaming. In a further separate coating step of the process a clear wear layer of composition D is applied to the foamable layer at approximately 100°C. The structure is then passed through a oven system to crosslink the layers at approximately 170°C and then expand the foam layer to approximately 200°C. The final cured, decorated and embossed product constitutes the floor covering material.

		<u>PHR</u>
A. ( <u>Saturant Layer</u> )		
	Exact 4038 MPO Resin	100
	Calcium Carbonate	66.7
20	Stearyl Methacrylate (settable plasticizer)	90
	Trimethylolpropane trimethacrylate (settable plasticizer)	10
	Lupersol 230 (free radical polymerisation initiator from Atochem)	5
25	Irganox 1010	0.1
	DSTDP	0.1
	Ultranox 626	0.05
B. ( <u>Backcoat Layer</u> )		
	Exact 4038	100
30	Calcium Carbonate	300
	Stearyl Methacrylate	90
	Trimethylolpropane trimethacrylate	10
	Lupersol 230	5
	Irganox 1010	0.1
35	DSTDP	0.1
	Ultranox 626	0.05

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C. ( <u>Foamable Layer</u> )		<u>PHR</u>
	Exact 5008	100
	Calcium Carbonate	66.7
	Stearyl Methacrylate	90
5	Trimethylolpropane trimethacrylate	10
	Lupersol 230	5
	Celogen OT (chemical Blowing agent from Uniroyal)	4
	Zinc Oxide	2
10	Luchem HA -B18	0.15
	Irganox 1010	0.1
	DSTDP	0.1
	Ultranox 626	0.05
D. ( <u>Wear Layer</u> )		<u>PHR</u>
15	Exact 3017	100
	Stearyl Methacrylate	70
	Trimethylolpropane trimethacrylate	30
	Lupersol 230	5
	Vinyl trimethosilane	4
20	Luchem HA -B18	0.3
	Irganox 1010	0.1
	DSTDP	0.1
	Ultranox 626	0.05



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CLAIMS

1. A sheet material suitable for use in or as a floor covering and comprising a polyalkene resin in intimate admixture with at least one additive comprising a filler, wherein said polyalkene resin has a relatively narrow molecular weight distribution (MWD) and, a small amount of long chain branching and produced by a single site catalysed polymerisation of at least one, linear, branched or cyclic, alkene having from 2 to 20 carbon atoms.
2. A sheet material according to claim 1 wherein said polyalkene is one having the following characteristics:
- a) Melt Index (MI) of from 0.1 to 100
  - b) Density of from 0.86 to 0.97; and
  - c) a DRI of from 0.1 to 6.0, preferably from 0.4 to 5.5.
3. A sheet material suitable for use in or as a floor covering and comprising a polyalkene resin in intimate admixture with at least one additive comprising a filler, wherein said polyalkene resin has a relatively narrow molecular weight distribution (MWD) and, a small amount of long chain branching and produced by a single site catalysed polymerisation and having the following characteristics:
- a) Melt Index (MI) of from 0.1 to 100
  - b) Density of from 0.86 to 0.97; and
  - c) a DRI of from 0.1 to 6.0, preferably from 0.4 to 5.5.
4. A sheet material according to any one of claims 1 to 3 wherein said polyalkene comprises a copolymer produced by copolymerisation of at least two alkenes comprising a first, linear or branched, alkene having from 2 to 8 carbon atoms and, at least one further, linear, branched or cyclic, alkene having from 2 to 20 carbon atoms.
5. A sheet material according to claim 4 wherein said first monomer comprises ethylene and said further monomer is selected from butene-1, hexene-1, and norbornene.
6. A sheet material according to claim 4 or claim 5 wherei:

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is used up to 15 mole percent of said further monomer(s).

7. A sheet material according to any one of the preceding claims wherein said sheet material comprises an, at least semi-, interpenetrating network of said polyalkene and a  
5 polymer of a selectively polymerisable liquid plasticiser monomer system which is substantially non-polymerisable under sheet forming conditions used in floor covering sheet material manufacture whilst being substantially  
10 polymerisable subsequently so as to produce a material substantially free of liquid plasticiser.

8. A sheet material according to claim 5 wherein said plasticiser monomer comprises a linear, branched or cyclic alkene having at least 10 carbon atoms and a polymerisable terminal functional group.

15 9. A polymer resin-based floor covering comprising at least one layer of a sheet material according to any one of claims 1 to 8.

10. A floor covering according to claim 9 which has a plurality of layers comprising a structural layer comprising  
20 a reinforcing carrier or substrate impregnated and/or coated with a saturant formula; a solid backcoat layer; and a clear protective or topcoat layer.

11. A process for the production of a sheet material suitable for use in or as a floor covering which process  
25 comprises the steps of:  
providing a polyalkene resin in accordance with any one of the preceding claims and at least one additive comprising a filler ;  
bringing said polyalkene resin into intimate admixture with  
30 said at least one additive in a high shear mixer for a period of at least 10 minutes at an elevated temperature of at least 75°C for melting the polyalkenes and sufficient to bring the mixture into a substantially fluid state without substantial degradation of the mixture;

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forming the fluid mixture into a sheet form; and allowing said sheet to cool and solidify.

12. A process according to claim 11 which includes the step of incorporating into the mixture a sheet formation  
5 processing aid.

13. A process according to claim 11 or claim 12 wherein the sheet forming process step comprises spread coating.

14. A process according to claim 13 wherein is used a liquid plasticiser spread coating aid.

10 15. A process according to claim 14 wherein is used a liquid paraffin spread coating aid.

16. A process according to any one of claims 12 to 14 wherein is used a selectively polymerisable liquid plasticiser monomer system which is substantially non-  
15 polymerisable under sheet forming conditions used in floor covering sheet material manufacture whilst being substantially polymerisable subsequently so as to produce a material substantially free of liquid plasticiser.

17. A process according to claim 16 which process includes  
20 the step of treating the sheet form material so as to induce polymerisation of said liquid plasticiser monomer system thereby to produce a sheet material substantially free of liquid plasticiser.

18. A process according to claim 17 wherein said sheet  
25 forming step is carried out at from 70 to 120 °C and said polymerisation step is carried out at from 150 to 250 °C.

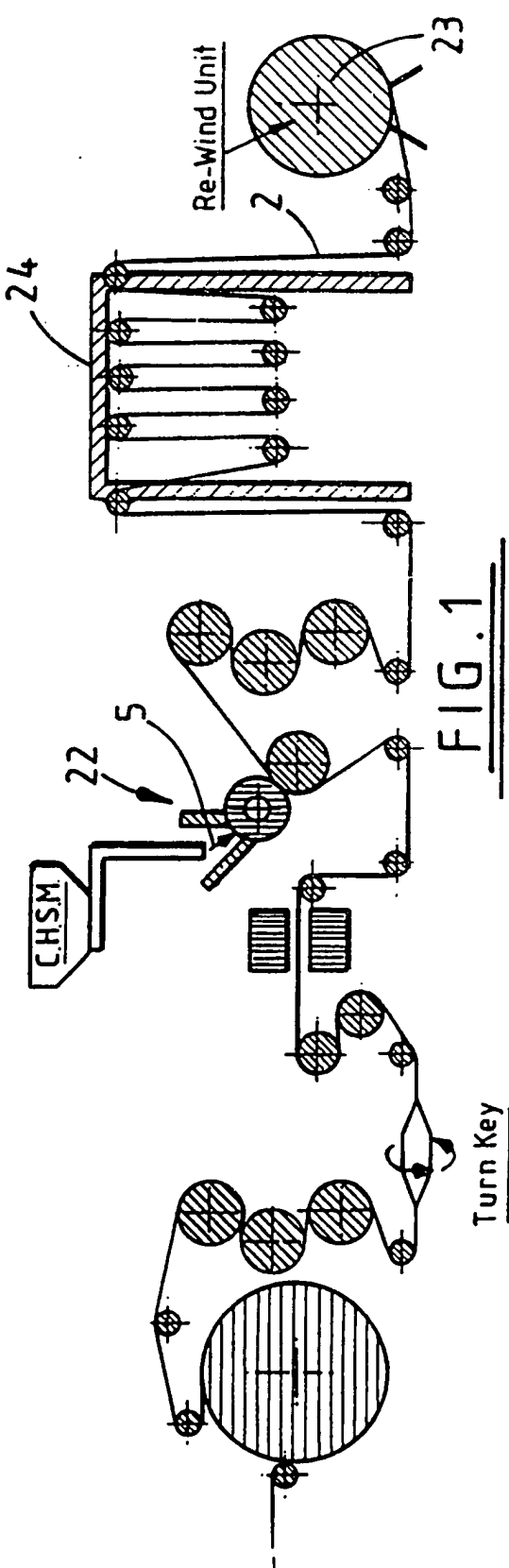
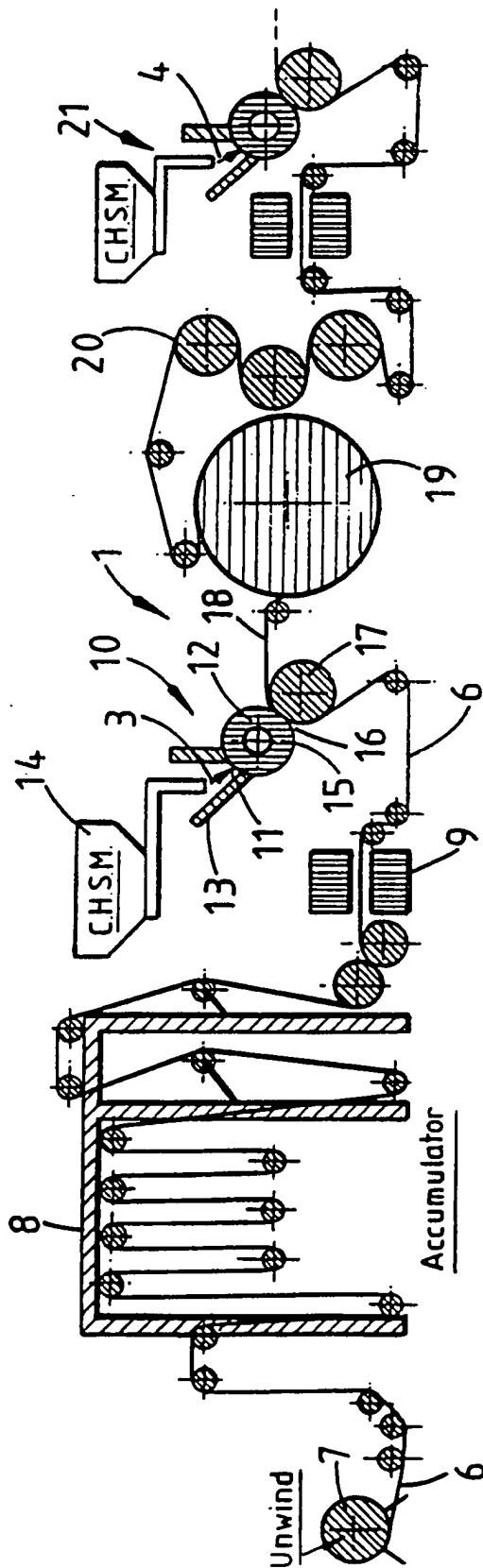
19. A process for the production of a floor covering comprising a plurality of layers comprising a structural layer comprising a reinforcing carrier or substrate  
30 impregnated and/or coated with a saturant formula; a solid backcoat layer; and a clear protective or topcoat layer, in

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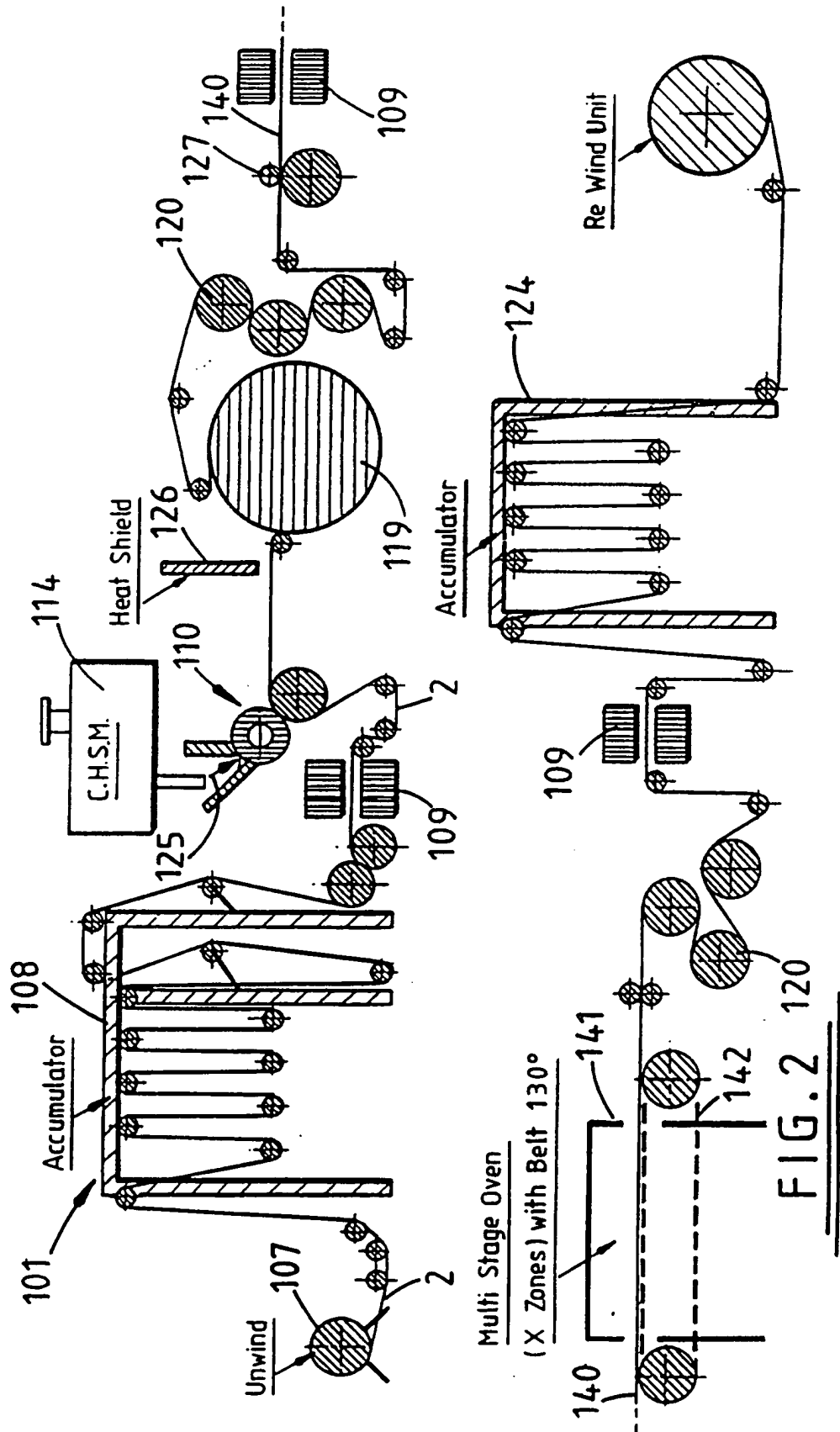
which process at least one of said layers is produced by a process according to any one of claims 11 to 18.

20. A process according to claim 19 for the production of a floor covering including at least one layer which is foamed,  
5 which process includes the step of producing a said foamed layer.

1-2



2-2



## INTERNATIONAL SEARCH REPORT

Intern. Application No.

PCT/GB 95/01855

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 D06N7/00 C08K3/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08K D06N C08J C09D C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 605 831 (MITSUBISHI PETROCHEMICAL CO) 13 July 1994 see page 5, line 28 - line 35; claims 1,22 see page 6, line 21 - line 29	1,4-6
A	see page 10, line 16 - line 51 ---	11
X	WO,A,94 09060 (DOW CHEMICAL CO) 28 April 1994 see page 11, line 35 - page 13, line 36; claims 1,16,18 see page 15, line 27 - line 35 see page 19, line 28 - page 20, line 7 see page 21, line 7 - line 14 -----	1-6

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

## \* Special categories of cited documents:

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Date of the actual completion of the international search

19 October 1995

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 95/01855

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
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		US-A-	5385972	31-01-95
		JP-A-	7026076	27-01-95
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WO-A-9409060	28-04-94	CA-A-	2145644	28-04-94
		EP-A-	0665863	09-08-95
		FI-A-	951799	13-04-95
		US-A-	5395471	07-03-95
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